5 (3)
AUTHORS:

Frolov, V. M., Krylov, O. V.,   SOV/20-126-1-29/62
Roginskiy, S. Z., Corresponding Member,
AS USSR

TITLE: Catalytic Dehydrogenation of Ethanol on Germanium
(Katalititheskoye degidrirovaniye etanola na germanii)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 1, pp 107 - 110
(USSR)

ABSTRACT:

Germanium is able to catalyze several redox reactions (Refs 1,2). The authors wanted to investigate the kinetics of some of these reactions in the case of various Ge-samples with different conductivity in the case of a concentration change of the current carriers within a wide range. This can facilitate the understanding of the mechanism of the semiconductor catalysis. The kinetics of the reaction mentioned in the title was investigated under static vacuum conditions in a quartz reactor. Powder with a specific surface of 0.05 - 0.1 m^2/g obtained by pulverization in the mortar in air served for this purpose. The Ge-powder was trained before the experiment at 850° or at 650°

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and at 10^{-5} - 10^{-6} torr. The mentioned dehydrogenation was investigated at 200-270°. A reduction of the reaction rate (Figs 1:1-4 cursive) took place in the case of subsequently carried

out ethanol compositions on Ge, trained at 850°. This was stopped after the fourth experiment. Beside hydrogen and acetaldehyde also ethylene was found to exist in the gas phase. Its content was reduced from experiment to experiment. The hydrogen pressure was in all experiments equal to the summed pressure of acetaldehyde and ethylene (accuracy 2-3%). The authors assume that the fresh Ge-surface adsorbs an oxygen molecule from ethanol (reaction I) thanks to its great affinity to oxygen. The covering of the Ge-surface with adsorbed oxygen leads to the breaking-off of the reaction (I). As late as from the fourth experiment on only the process of the catalytic dehydrogenation takes place on the Ge-powder. The chemosorption of oxygen was carried out after the fourth experiment in order to clarify the effect of a complete covering of the Ge-surface with oxygen. The curves 5-8 (Fig 1) belong to the subsequently carried out experiments. They describe the kinetics of the hydrogen separa-

Card 2/4   tion under the given conditions. Since the pressure of the

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acetaldehyde formed on the oxidized surface surpasses consider-
ably the hydrogen pressure the removal of the adsorbed oxygen
according to the reaction (III) is to be assumed. The catalytic
reaction (II) proceeds then on the surface free from oxygen.
Thus, adsorbed oxygen can in the case of the system germanium-
-ethanol approach to the stationary activity of the catalytic
dehydrogenation from the side of the surface free from oxygen
as well as from the side of the surface completely covered by
the adsorbed oxygen. Figure 1 shows the electronic character-
istics of the alloyed Ge-samples, the logarithm of the pre-ex-
ponential multiplier (k_o) and of the seeming activation energy
(E) of the catalytic ethanol dehydrogenation. The results des-
cribed clarify to a certain extent the often discussed problem
of the catalytic equivalence of the p- and n-semiconductors.
The authors assume with a certain security with respect to the
reaction mentioned in the title that the activation energies on
the p-germanium are considerably lower than on n-germanium.
This conclusion does, however, not hold in the case of all other
reactions (Refs 6,7). The range of the investigated systems is
to be widened and the catalytic processes are to be more tho-

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roughly investigated. Data concerning the change of the electronic characteristics of the surface during the reaction process are to be used. There are 3 figures, 1 table, and 7 references, 4 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences, USSR)

SUBMITTED: January 28, 1959

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SOV/20-126-4-35/62

AUTHOR: Roginskiy, S. Z., Corresponding Member, Academy of Sciences, USSR

TITLE: The Kinetics of Semiconductor Catalysis With Controlled Chemisorption (Kinetika poluprovodnikovogo kataliza pri kontrole khemosorbtsiyey)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 4, pp 817-820 (USSR)

ABSTRACT: The author investigated the irreversible process $A + B \longrightarrow AB$ which proceeds according to the scheme $A \xrightarrow{1} A_{chem} \xrightarrow[2]{+ B_{gas}} AB_{chem} \xrightarrow{3} AB$ in which each arbitrary phase may be employed for control. A series of peculiarities of the kinetics of semiconductor catalysis occurs already in the most simple case if the reaction proceeds under control of chemisorption of one of the initial substances, for instance A. The composition of the activated complex $\lceil K \rceil$ is determined by the final result of this phase and by the type of the active centers participating in the adsorption. For a group of i equal partial sections the

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. The Kinetics of Semiconductor Catalysis With Controlled Chemisorption

rate w_i may be expressed by the following equation:

$$w_i = -dn_{A_i}/dt = -bd[A]_i/dt = bd[AB]/dt = \sqrt{s}K_i^{\#}[X_i][A], \quad (1)$$

where n_A is the number of molecules A in the volume; $[A]$ is the concentration of A-molecules, $[AB]$ is the concentration of molecules of the reaction products. The ratio s of the surface to the volume of the reactor is included in the coefficient b. denotes the frequency of conversion of the activated complex into completely chemisorbed molecules. $[X_i]$ is the concentration of the i-th centers which are contained in $[K]$; $K_i^{\#}$ is the equilibrium constant for $[K]$ according to equation (2a):

$$(2a) \quad K_i^{\#} = \exp\left[(RT)^{-1}(-F_i^{\#}(\Delta V=0) - e\Delta V_i^{\#} \pm e\Sigma\Delta V)\right] =$$

$$= \exp\left[(RT)^{-1}(-F_i^{\#})\right] = K_{oi}^{\#}M_v, \text{ where } M_v = \exp\left[(RT)^{-1}(e\Delta V_i^{\#} \pm e\Sigma\Delta V)\right]. \quad (2b) \quad F_i^{\#}(\Delta V=0) \text{ is the free energy of formation of}$$

$[K]$ at $\Delta V=0$; $\Delta V_i^{\#}$ is the electric surface potential conditioned

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by $[K]$; $\Sigma \Delta V$ is the electric potential caused by all completely adsorbed molecules. M_v does not differ much from 1. Equation (1) may be written down as follows: $w_i = \sqrt{s} K_{oi}^* [X_i][A] M_v$ (1a)

The present paper discusses the kinetic connections related to the individual factors of this equation. There are 10 references, 8 of which are Soviet.

SUBMITTED: February 4, 1959

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Robinsky, S. Z.

MALAKHV, Aleksey A. - "On the theory of contact catalysis of hydrogenation and dehydrogenation reactions." (Section I)

BORESKOV, Georgy K., and VASILEVICH, A. A. - "Mechanism of isotope exchange of hydrogen on platinum" (Section I)

FRIUS, T. (probably Yakov T. EIDUS) - "On the role of intermediate surface forms in some heterogeneous-catalytic reactions of carbon monoxide and olefins" (Section I)

FATKIN, Lev D, and GORCHKOV, V. L. - "Catalytic transformation of cyclohexane and copper and the multiplier theory" (Section II)

MARSALLEVN, Yusuf G., and GUSEYNOV, M. M. - "Chlorocarbons manufacture by chlorination of alkanes in the fluid bed of a catalyst" (Section III)

KUKLAREV, L. A. - "Specific aspects of the catalysis by complex compounds" (Section II)

FEDEVSKAYA, Yu. I., KLLASKY, V. B., and VOLKOVSKIY, V.V. - "Investigation of heterogeneous catalysts by electron spin resonance" (Section II)

FRDOV, A. D. - "On the catalytic synthesis of organosilica compounds" (Section III)

BOLESKY, Simon L. - "Electronic effects in catalysis" (Section I or II)

BRIDGMAN, A. N. - "The structure and texture of Chromia-alumina-potassium oxide catalysts" (Section II)

HAVLIN, N. I., and BEL'SKII, I. P. - "Catalytic transformations in the furanic compound group" (Section III)

OSHINSKY, D. V., and SIMONOVA, V. P. - "Kinetic and mechanism of catalytic reduction in aromatic nitro derivatives" (Section I)

KROTOV, A, and KOTEV, A - "Active sites on transition metal catalysts, revealed in the infrared spectra of adsorbed NO." (Section II)

YOCHIKWA, L V., ARTIFINA, T. V., and LEE HE HENN (Possibly Li Ho-seng, Moscow Textile Institute) - "The effects of structural characteristics of porous catalysts on activity and kinetic behavior of heterogeneous-catalytic reactions" (Section I)

VOLKOKEKTN, T. - "General ideas on the electronic theory in catalysis on semiconductors" (Section I)

YERTOV, B. V., and KHIPUNOVA, N. F. - "Catalytic transformation of cyclohexane and copper and the multiplier theory" (Section II)

reports to be presented at the 2nd Intl Congress on Catalysis, Paris, France, 4-9 Jul '60.

PHASE I BOOK EXPLOITATION   SOV/4186

Akademiya nauk SSSR

Stroyeniye veshchestva i spektroskopiya (Structure of Matter
    and Spectroscopy) Moscow, Izd-vo AN SSSR, 1960. 113 p.
    Errata slip inserted. 2,300 copies printed.

Ed.: K. V. Astakhov, Professor;   Tech. Ed.: T. P. Polenova.

PURPOSE: This collection of articles is intended for physicists
    and chemists interested in spectroscopic methods of research
    on the structure of molecules and related problems.

COVERAGE: The articles contained in this collection were
    taken from the editorial files of the Zhurnal fizicheskoy
    khimii (Journal of Physical Chemistry) and are concerned
    with spectroscopic methods in research on the structure of
    molecules, the hydrogen bond, isotopic effects, problems
    in magnetochemistry, the structure of aqueous solutions of
    electrolytes, and the chemistry of complex compounds. Refer-
    ences accompany individual articles.

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Structure of Matter and Spectroscopy   SOV/4186

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Shigorin, D. N., M. M. Shemyakin, M. N. Kolosov, and T. S. Ryabchikova [Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov] and Institut biologicheskoy i meditsinskoy khimii AMN SSSR [Institute of Biological and Medical Chemistry of the Academy of Medical Sciences USSR]. Intermolecular Interaction and Oscillation Spectra of Acetylene Compounds   36

Izmail'skiy, V.A., and V.Ye. Limanov [Moskovskiy pedagogicheskiy institut im. V.P. Potemkina-Moscow Pedagogical Institute im. V.P. Potemkin] Absorption Spectra of Derivatives of N-[β- (4-Nitrophenyl)-Ethyl]- Aniline   41

Izmail'skiy, V. A., and V. Ye. Limanov [Moskovskiy pedagogicheskiy institut im. V. P. Potemkina (Moscow Pedagogical Institute imeni V. P. Potemkin)]. Absorption Spectra of Derivatives of N-[β-(2,4-Dinitrophenyl)-Ethyl]-Aniline   53

Rabinovich, I. B. [Gor'kovskiy gosudarstvennyy universitet im. N. I. Lobachevskiy [Gor'kiy State University imeni N. I. Lobachevskiy]. Effect of Displacement of Hydrogen by Deuterium on the Molal Volume of Liquids   62

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Yesin, O. A. [Ural'skiy politekhnicheskiy institut im.
S. M. Kirova Sverdlovsk (Ural Polytechnic Institute imeni
S. M. Kirov, Sverdlovsk)]. Form of Surface Tension
Isotherms   111

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Card 6/6   10-20-60

ROGINSKIY, S.Z.

Electronic factors in semiconductor catalysis and rules for the selection of catalysts. Probl. kin. i kat. 10:5-20 '60.

(MIRA 14:5)

1. Institut fizicheskoy khimii AN SSSR.
(Semiconductors)   (Catalysts)

FROLOV, V.M.; KRYLOV, O.V.; ROGINSKIY, S.Z.

Catalytic properties of germanium. Probl. kin. i kat. 10:102-107
'60.   (MIRA 14:5)

1. Institut fizicheskoy khimii AN SSSR.
                         (Germanium)

KRYLOV, O.V.; ROGINSKIY, S.Z.; FOKINA, Ye.A.

Catalysis on semiconductors in the region of natural conduction.
Probl. kin. i kat. 10:117-120 '60.   (MIRA 14:5)

1. Institut fizicheskoy khimii AN SSSR.
                    (Catalysis)   (Semiconductors)

ROGINSKIY, S.Z.; SINYAK, Yu.Ye.; YANOVSKIY, M.I.

Investigation of the surface of an alkali promoter of the ammonia
catalyst by means of the isotopic method. Probl. kin. i kat.
10:210-213 '60.   (MIRA 14:5)

1. Institut fizicheskoy khimii AN SSSR.
          (Catalysts) (Alkali metal oxides) (Alkaline earths)

S/081/60/000/021/007/018
A005/A001

Translation from: Referativnyy zhurnal, Khimiya, 1960, No. 21, p. 50, # 83985

AUTHORS: Andrianova, T. I., Roginskiy, S. Z.

TITLE: An Experimental Investigation of Correspondence Between the Homogeneous and Heterogeneous Acid-Basic Catalyses

PERIODICAL: Probl. kinetiki i kataliza, 1960, Vol. 10, pp. 298-302

TEXT: The authors show that the acid anhydrides of transition elements (Cr_2O_3, V_2O_5) are not superior to acid anhydrides of non-transitional elements in the etherification of the acetic acid and the hydrolysis of the esters. The commercial aluminum silicate catalyst containing at its surface acid centers of great power excels the rest of the investigated acid catalysts in the studied reactions in the gaseous phase. For heterogeneous reactions of the acid type in the liquid phase, the resin $KY-2$ (KU-2) considerably excels the aluminum silicate. The decomposition of alcohols, the hydrolysis of esters, and the condensation of carbonyl compounds can be proceeded on acid as well as on basic catalysts, which gives the reason to refer these reactions to the category of the general acid-basic

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A005/A001

An Experimental Investigation of Correspondence Between the Homogeneous and Hetero-
geneous Acid-Basic Catalysis

catalysis. It can be assumed, as some special reactions show, that the conclusion
is justified on the far-reaching analogy between the homogeneous and heterogeneous
catalyses. Nevertheless, for the practical selection of the catalyst for a definite
reaction, some additional demands must be taken into account, in the first place
the selectivity.

From the summary of the authors.

Translator's note: This is the full translation of the original Russian abstract.

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VARSHAVSKIY, Ya.M., doktor khimicheskikh nauk; ROGINSKIY, S.Z.; SHNOL',
S.E., kand.biologicheskikh nauk

Isotopes in biochemistry. Zhur.VKHO 6 no.3:275-284 '61.

(Radioisotopes)   (Biochemistry)   (MIRA 14:6)

ROGINSKIY, S.Z.

    Role of consolidated chains in catalysis. Probl. kin. i kat.
    10:373-380 '60.   (MIRA 14:5)

    1. Institut fizicheskoy khimii AN SSSR.
                            (Catalysis)

ROGINSKIY, S. Z.

Role of electronic factors in catalysis. Kin. i kat. 1 no.1:15-
31 My-Je '60.   (MIRA 13:8)

1. Institut fizicheskoy khimii Akademii nauk SSSR.
                        (Catalysis)

ROGINSKIY, S.Z,; YANOVSKIY, M.I.; LU PEY-CHZHAN; GAZIYEV, G.A.; ZHABROVA,
        G.M.; KADENATSI, B.M.; BRAZHNIKOV, V.V.; NEYMARK, I.Ye.;
        PIONTKOVSKAYA, M.A.

Chromatographic determination of the adsorption isotherms of
gases and of the specific surface of solids. Kin.i kat. 1
no.2:287-293 Jl-Ag '60.   (MIRA 13:8)

1. Institut fizicheskoy khimii AN SSSR.
            (Adsorption)

ROGINSKIY, S. Z.; AL'TSHULER, O. V.; YANOVSKIY, M. I.; MALININA, Ye. I.;
MOROKHOVETS, A. Ye.

Preparation of radioactive cesium concentrates by the use of
ion exchange glauconite columns. Radiokhimiia 2 no. 4:431-437
'60.
                                                    (MIRA 13:9)
          (Cesium--Isotopes)   (Glauconite)

ROGINSKIY, S. Z. ; MALININA, Ye. V.; YANOVSKIY, M. I. ; AL'TSHULER, O. V.;
MOROKHOVETS, A. Ye.

Preparation of concentrates of radioactive cesium isotopes on
heavy metal ferrocyanides precipitated from solutions with a
high content of extraneous salts. Radiokhimiia 2 no.4:438-445
'60.   (MIRA 13:9)

(Cesium—Isotopes)   (Ferrocyanides)

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9.4300 (1150,1158,1160)
5.4100   2209, 1043, 1273, 1136, ''

S/063/60/005/005/001/021
A051/A029

AUTHOR: Roginskiy, S.Z., Corresponding Member of the USSR Academy of
         Sciences

TITLE: The Chemistry of Semi-Conductors and Electronic Mechanisms of
        Chemical Reactions

PERIODICAL: Zhurnal Vsesoyuznogo Khimicheskogo Obshchestva im. D.I.
             Mendeleyeva, 1960, No. 5, Vol. 5, pp. 482-492

TEXT: The author describes how the significance of the chemical aspects in
the physics of semi-conductors grew with the development of this field and
mentions scientists, such as A.F. Ioffe (USSR) and V. Shottky (Germany),
who where amongst the first to recognize the importance of the chemistry
of solids in this connection. The basis for most of the practical appli-
cations of semi-conductors lies in the replacement of mechanical and electro-
technical instruments and special tubes with "crystallo-chemical construc-
tions", in which sections and layers having a special chemical and micro-

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chemical composition are created as a result of appropriate chemical pro-
cessing of the semi-conductor and which results in the solid body acquiring
certain electronic properties. Mechanical current rectifiers, vacuum tubes,
replaced successfully by solid rectifiers, are given as an example of this
stipulation. The action of the latter is based on the special properties
of the occurring potential barrier. Reference is further made to the prin-
ciple of semi-conductors used for the direct cooling with an electrical
current, i.e., semi-conductor refrigerators. This principle is based on
Peltier's heat absorption, when an electrical current passes in a given
direction through the border lines between N and P (electron-conducting
and hole-conducting, respectively,) conductors. In this case the electro-
conductivity is only slightly dependent on the temperature, which is a
characteristic of degenerated semi-conductors (semi-metals, Ref. 1). Ioffe
(Ref. 2) showed that the semi-conductor properties of solids depend on the
close-range order, which, in turn, is determined by the electronic type and

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degree of polarity of the chemical bond, the ratio of the particle radii,
which form the crystal lattice, and also by the presence and distribution
of the admixture atoms. A second cause for the development of the chemical
aspect is given as the inability of satisfying the physical requirements of
semi-conductors and their many forms of application in materials with cer-
tain electronic properties on the basis of only easily available and well-
studied substances. The study of the chemistry of rare elements and the
synthesis of new elements and compounds were the result. The discovery of
the group of binary and more complex semi-conductor iso-electronic analogies
of the elements of the IV group, of the general type $A^{III}B^V$, $A^{II}B^{VI}$, etc.,
are given as an example of the results of directing investigations toward
the chemical bond, to electronic characteristics of solid bodies, etc. The
characteristic feature of the so-called third stage of the chemical develop-
ment in the field of semi-conductors was the penetration of models and
theoretical and experimental methods of the physics of semi-conductors into

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the main sections of chemical theory. New conceptions arose on the
mechanism of the chemical transformation of solids and high-molecular com-
pounds and their reactivity. In the case of an ideal self(i)-conductor,
there are no admixture levels between the valency and conductivity strips.
The fraction U/kT is used to determine whether a body can be considered an
insulator or semi-conductor, where U is the width of the forbidden zone,
k the Boltzmann constant, T the absolute temperature. It is approximately
assumed that in self-conductivity and normal mobility of the charge
carriers the crystal behaves as a semi-conductor at U/kT less than 150 and as
a dielectric at U/kT more than 150. The energy spent on the formation of
charge carriers, as well as the mobility, characterizes the entire lattice
and not only an isolated atom. The excitons, first described by Ya.I.
Frenkel' (Ref. 3) are said to play an important role in the transportation
of the activation energy within the lattice and between its volume and sur-
face. Electrons and electron holes are the main charge carriers in semi-

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conductors and metals. Sections of the volume or surface of the lattice
which are potential depressions for the charge carriers play an important
role in certain physical processes in the semi-conductors, such as energy
dispersion in electroconductivity or luminescence. The internal photo-
effect which leads to the occurrence of electronic conductivity in insula-
tors, for example, is said to be due to the irradiation of semi-conductors
and insulators with light of a certain wave-length, which creates additional .
charge carriers and excitons in the crystals, their concentrations attain-
ing super-equilibrium. Primary photo-physical and radiation-chemical pro-
cesses are said to be accompanied by various chemical transformations in
semi-conductors. Fading of colors of certain organic dyes is given as an
example (Ref. 4). The chemical decomposition of azides is outlined as an
example of similar effects noted in many types of chemical processes, which
take place within the semi-conductor or on its surface. A detailed study
was made of the kinetics and mechanism of decomposition of inorganic and

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organic azides, since great practical significance is attached to some of
the compounds of this group, as initiating explosives, combined with the
simplicity of the products of reaction. For the inorganic azides the final
products are free metal and molecular nitrogen. The path taken by the
nitrogen in its photochemical decomposition, and forming N_2, is followed.
The scheme of the N_2 formation from the oxidation of N_3^- is given. The path
followed by the metal is also outlined. The importance of the exciton in
the photolysis is explained as facilitating the transfer of the electron
from the valency band to the conductivity band. Electrons, holes of con-
ductivity and excitons probably participate in the decomposition of azides
with X-rays and gamma rays, rapid electrons and heavy particles. The
described theory shows that the major stages of the azide decomposition are
significantly different from the usual homogeneous reactions. The spectro-
scopic study of the azides showed that energy of the edge of the absorption
strip corresponding to the formation of conductivity electrons according to

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the scheme $N_3^- + h\nu \longrightarrow N_3 + n$ decreases with a growth of the metal ionization energy (J), which takes part in the formation of the azide lattice, i.e., U decreases with a growth of J. The general picture obtained for the azides was found to be characteristic for the oxidation-reduction reactions of the phase types: Solid body 1 $\longrightarrow$ solid body 2 + gas, and solid body 1 + gas 1 $\longrightarrow$ solid body 2 + gas 2. Other processes in the solid phase are discussed. A similar primary process is said to be probable for the primary chemical stage of the decomposition of many salts, the anions of which, in the neutral state, are unstable (Ref. 8), for example for oxalates, $C_2O_4^{2-} \longrightarrow C_2O_4 + 2n \longrightarrow 2CO + 2n$. Similar electron-excitation mechanisms are expected for basic reactions in the formation of metals, by the reduction of oxides, sulfides, etc. The author points out that the entire modern theory and practice for controlling the properties of the emulsion of silver halides, applicable to the usual photographic process, roentgenography, electron recording in electron apparatus, to radiography, etc., is

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based on the semi-conductor process mechanisms which are not gone into in
this article. A discussion follows of the electronic mechanisms of hetero-
geneous catalysis on semi-conductors. Only the main laws and initial re-
gularities of the subject are given, based on (Ref. 9-12). Semi-conductors
are said to be dominant as the latest solid catalysts of the oxidation-re-
duction reactions in the gaseous and liquid phases. A high correlation is
present between their catalytic and electron-physical properties. A new
effect noted also in other types of surface-chemical reactions is the effect
on the rate, kinetics and selectivity of processes, which is due to the
electrical charging of the surface of the semi-conductor in relation to its
volume (Ref. 17-18). According to Ref. 18, the charging, in combination with
the heterogeneous nature of the surface, determines the final form of the
kinetic equations of catalytic and chemosorption processes. The work per-
formed on the electron emission, which is a starting point in all physical
phenomena associated with the electron emission or with their redistribution

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between the various phases and layers, appears to be one of the main factors
of semi-conductor catalysis (Ref. 24). The author states that in a usual
semi-conductor catalysis and in catalysis on semi-conductors when irradiated
with light, distance effects can be obtained. Characteristic distance
effects are noted in semi-conductor catalysis when the catalysts are irra-
diated with light during the process. In oxidation-reduction catalysis on
semi-conductors free electrons and holes of the surface take an active part.
The chemical bonds which are formed in chemosorption and catalysis in active
sections have been more clearly investigated as result of studies made on
spectral, electronic and magnetic methods of investigations. The interest-
ing results of these investigations are not dealt with in this article.
The biochemical processes are discussed in the following sequence: general
features, mechanisms of photosynthesis, low-temperature polymerization.
The author points out here that semi-conductivity is a phenomenon not only
of inorganic substances with a crystalline structure, but also of liquids

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The Chemistry of Semi-Conductors and Electronic Mechanisms of Chemical
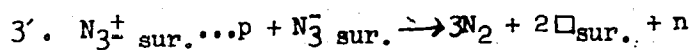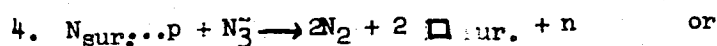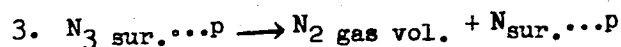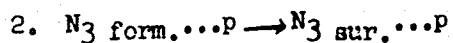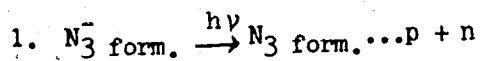Reactions

and organic substances. The biological photosynthesis is used as an
example for illustrating the penetration of semi-conductor theories into
biology, bio-chemistry and biophysics. A new vast region for the applica-
tion of semi-conductor processes was found in radiation chemistry of con-
densated systems, in polymerization, reactions of free radicals, and in
chemistry of low-temperatures. The question is raised as to the probabili-
ty of these mechanisms occurring in ordinary organic reactions. It is
pointed out that only the close-range order is required for semi-conductor
phenomena to occur, as well as the collectivization of charge carriers in
the conductivity strip. The author is inclined to believe that in all cases
where the organic chemist deals with complex conjugated bonds, the semi-
conductor approach is a lawful addition to the more traditional chemical
approach. There are 51 references: 36 are Soviet, 12 English, 3 German.

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S/063/60/005/005/001/021
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The Chemistry of Semi-Conductors and Electronic Mechanisms of Chemical Reactions

$$1. \quad N_3^- \text{ form. } \xrightarrow{h\nu} N_3 \text{ form.} \cdots p + n$$

$$2. \quad N_3 \text{ form.} \cdots p \longrightarrow N_3 \text{ sur.} \cdots p$$

$$3. \quad N_3 \text{ sur.} \cdots p \longrightarrow N_2 \text{ gas vol. } + N_{\text{sur.}} \cdots p$$

$$4. \quad N_{\text{sur.}} \cdots p + N_3^- \longrightarrow 2N_2 + 2 \, \square \, \text{sur. } + n \qquad \text{or}$$

$$3'. \quad N_3^{\pm} \text{ sur.} \cdots p + N_3^- \text{ sur.} \longrightarrow 3N_2 + 2\square_{\text{sur.}} + n$$

where $\square$ is the designation for the neutral anion vacany.

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$S.\,1190$

5(4)

67957

SOV/20-130-1-35/69

AUTHOR: Roginskiy, S. Z., Corresponding Member AS USSR

TITLE: On the Origin of the Pre-sorption Effect and on Some Other
            Anomalies of Catalytic Oxidation of CO on Oxide-Semiconductors

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 1, pp 122-125 (USSR)

ABSTRACT: The author explains the processes in the oxidation of CO on oxide
            semiconductors by means of the band model semiconductor (SC). He
            discusses the varying course of CO-sorption in the presence and
            in the absence of oxygen. The increase in the work function φ
            due to O is based on the reduction of the band deformation due
            to self-charging of the surface of SC surface in the chemo-
            sorption of CO. An equation is deduced and discussed for the
            influence of O on φ and for the energy E_{chem} of chemosorption.

            The observed pre-sorption effect is traced back to the
            positively modifying effect of the adsorbed oxygen. The influence
            $\Delta\varphi$ of the acceptor gas on the band deformation increases when a
            downward deformation existed at the beginning, whereas it
            decreases in the reverse case (Fig 1). The modifying effect of O
            is therefore intensified by additions which reduce the work

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On the Origin of the Pre-sorption Effect and

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SOV/20-130-1-35/69

on Some Other Anomalies of Catalytic Oxidation of CO on Oxide-Semiconductors

function, on the other hand, it is inhibited by additions which increase φ . At low total pressure of the reacting gas mixture and at high temperatures the pre-sorption effect is bound to disappear. The same takes place when the band deformation of SC is compensated by an electric field or when the chemosorption- and the catalysis rate are adapted (Fig 2). The inhibiting effect of water vapor on CO-oxidation is explained by the increase of the Fermi level due to the surface charge of SC (Ref 13) observed by V. I. Lyashenko, and as a result of the intensive adsorption of H_2O. Figure 3 shows the modifying

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On the Origin of the Pre-sorption Effect and   SOV/20-130-1-35/69
on Some Other Anomalies of Catalytic Oxidation of CO on Oxide-Semiconductors

effect of additions (Li to NiO and ZnO). An almost complete
correlation exists between the changes of φ and E_{cat}
(= activation energy of catalysis). There are 3 figures and
18 references, 15 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute of Physical Chemistry of the Academy of Sciences,
USSR)

SUBMITTED: July 13, 1959

Card 3/3

$\frac{5(4)}{5}$ 5.4300

SOV/20-130-2-35/69

AUTHORS: Roginskiy, S. Z., Corresponding Member AS USSR, Khait, Yu. L.

TITLE: The Problem of the Origin of the Compensation Effect in Chemical Kinetics

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 2, pp 366 - 369 (USSR)

ABSTRACT: Several research workers (Refs 1-3) found when comparing the activity of catalyzers that the relation $\ln k_0 =$ const $+ \beta E$ exists between the coefficients k_0 and E of the Arrhenius-equation $k = k_0 \exp(-E/RT)$. Similar results were obtained by the first-mentioned author in collaboration with L. V. Rozenkevich (Ref 4). This compensation effect occurs mainly in reactions with condensed phases. G. M. Zhabrova (Ref 1) set up the equation: $\ln k_0 =$ const$+ \beta E^n$, where n is between 1 and 3. After a survey of publications dealing with this subject and mentioning a paper by L. D. Landau (Ref 15), the authors make an attempt at explaining the compensation effect. For this purpose, they proceed from a

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The Problem of the Origin of the Compensation Effect SOV/20-130-2-35/69
in Chemical Kinetics

statistical method of calculating the velocity of activation
processes on solid phases, which was developed by the se-
cond-mentioned author (Ref 17). The activation process thus
consists of a finite number of elementary events. Each of
these events is due to the fact that the energy E' which
equals a critical value $E \gtrless kT$ or exceeds this value, happens
to concentrate in a volume d^3 which has the magnitude of a
particle volume, the energy in the surrounding volume 1^3
being correspondingly reduced. The compensation effect might
be based upon the probability of the concentration of an ex-
cess energy $E' \gtrless E \gg kT$ depending on the local temperature
in that volume 1^3 in which the elementary event takes place,
There are 19 references, 14 of which are Soviet.

SUBMITTED: August 6, 1959

Card 2/2

AUTHORS: Roginskiy, S. Z., Corresponding
Member AS USSR, Shishkin, V. A.

67944

S/020/60/130/03/026/065
B004/B011

TITLE: Investigation of the Adsorption of Unsaturated Carbon Fluorides
C_2F_4 and C_3F_6 in the Electron Projector

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 3, pp 577-580
(USSR)

ABSTRACT: The authors refer to publications (Refs 1-4) dealing with the
discrete bright spots becoming visible on the screen of an
electron projector at a gas pressure of 10^{-6} - 10^{-5} torr. They
discuss the explanations given by other scientists and in this
connection quote I. I. Tret'yakov (Ref 3) who found out that in
the case of small gas molecules there is a connection between
the electronic structure of their molecules and the shape of
the spots. S. Z. Roginskiy (Ref 4) set up a hypothesis, accord-
ing to which the π-electrons of the double bonds take part in
the formation of spots, in which connection the bound biradicals
formed with adsorption play the principal part. In the present
paper, this hypothesis was checked by means of chemically
inert unsaturated carbon fluorides. The gases C_2F_4 and C_3F_6

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Investigation of the Adsorption of Unsaturated
Carbon Fluorides C_2F_4 and C_3F_6 in the Electron
Projector

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B004/B011

were offered by Academician I. L. Knunyants. The experimental
part describes the regulation of the desired gas pressure in
the range $10^{-2} - 10^{-7}$ torr by means of active carbon. The
pictures of such spots are shown in figures 1-4. The following
conclusions are drawn: 1) the connection between the appearance
of double spots and rings on the one hand, and the double bond
on the other, is confirmed. The phenomenon can be repeated
several times without the addition of new gas amounts.
2) It was not confirmed that micropoints must by all means par-
ticipate in the formation of molecule images; 3) Rings were ob-
served only in the case of the less symmetrical C_3F_6 molecules.

4) The clearness of the molecule images and their lifetime rise
with dropping temperature, in which connection the change in
the images is well observable. 5) The data obtained do not
contradict the hypothesis of a radicalization of the π-bonds.
The formation of such radicals by the separation of the π-bond
is possible both before adsorption, in the space around the
point, and in adsorbed molecules. 6) The geometrical inter-
pretations of the images and of their changes shown in

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Investigation of the Adsorption of Unsaturated
Carbon Fluorides C_2F_4 and C_3F_6 in the Electron
Projector

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B004/B011

references 1,2, are insufficient. From the fact that molecules
differing as to structure, yield well reproducible images of
the same form it may be concluded that a complicated relation-
ship exists between the image form and the electronic structure
of the molecule. It is assumed that the molecule images re-
produce the probability of the distribution of the electron
cloud of such electron shells as participate in the π-bond.
The low chemosorption character of the molecules investigated
allows the conclusion that the separate bonds remain localized
on the molecules. The authors thank I. A. Bespalova for his
collaboration. There are 4 figures and 6 references, 4 of
which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of
                Physical Chemistry of the Academy of Sciences, USSR)

SUBMITTED: July 9, 1959

Card 3/3

Roginskiy, S Z

11.5000
5.1190

81870
S/020/60/133/02/46/068
B004/B064

AUTHORS: Khuan Yu-mey, Keyer, N. P., Roginskiy, S. Z.,
Corresponding Member AS USSR

TITLE: Investigation of the Catalytic Decomposition of Hydrazine on Nickel Sulfide and on Its Solid Solutions

TEXT: While the relationship between the electrical properties and the catalytic and adsorption properties of metallic oxides has been investigated in many previous papers (Refs. 1-3) no such papers exist as regards metallic sulfides. In their investigations the authors used NiS in order to study the effect of various additions of non-bivalent metal sulfides (Li_2S, In_2S_3) and to compare them with the behavior of NiO (with additions of Li_2O and In_2O_3). The nickel sulfide was obtained from $NiCO_3$ (i.e. $NiCO_3$ + Li_2CO_3, $NiCO_3$ + $In(NO_3)_3$) by passing

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Investigation of the Catalytic Decomposition of   81870
Hydrazine on Nickel Sulfide and on Its Solid   S/020/60/133/02/46/068
Solutions   B004/B064

through H_2S at $450^\circ C$. The X-ray analysis made by M. Ya. Kushnerev showed
that NiS was obtained as β-form with a hexagonal crystal structure. The
specific surface was determined with the equilibrium isotherm of the ad-
sorption of krypton at $-195^\circ C$ according to Brunauer, Emmet, and Teller.
The tablets formed from the NiS powder at 4000 atm had a resistance of
1.2 ohm.cm which increased in the range of $78-573^\circ K$ in accordance with a
rise in temperature. It can therefore be said that within this sphere
NiS possesses metallic conductivity. A measurement of the thermo-emf
showed that NiS is a semiconductor of the n-type. The decomposition of
hydrazine occurs at 1 torr in accordance with the reaction equation
$3N_2H_4 \rightarrow N_2 + 4NH_3$. In nickel oxide it is accelerated by adding Li_2O,
while it is retarded by adding In_2O_3 (Fig. 1). In the experiments with

NiS palladium was used in order to check whether hydrogen was liberated.
Since this was not the case the reaction proceeded according to the
above equation. The kinetics of the reaction was investigated by mea-
suring the nascent nitrogen. Fig. 2 shows the kinetic isotherms of the

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Investigation of the Catalytic Decomposition of   S/020/60/133/02/46/068
Hydrazine on Nickel Sulfide and on Its Solid   B004/B064
Solutions

decomposition of N_2H_4 at 60, 75, and $100^\circ C$ in the coordinates
$\log(-\Delta P_{N_2H_4})$, $\log t$. Fig. 3 shows the dependence of the composition of t
and $P_{N_2H_4}$. The speed of the reaction increases from $60-150^\circ C$ and de-
creases after $150^\circ C$. The assumption that this is due to a poisoning of
NiS by NH_3 was proved by pre-treating NiS with NH_3. NH_3 retards the reac-
tion. Fig. 4 shows the isotherms of the reaction at $75^\circ C$ and with addi-
tions of 0.2 - 1.0 at% of Li or 0.2 - 1.0 at% of In to NiS. Furthermore,
the dependence of the speed of the reaction on these additions is shown.
In the case of an addition of 0.2 at% of Li the maximum rate was observed
which is the same as the maximum rate of dependence of the work function
on Li or In addition as measured by E. Kh. Yenikeyev. In general the ef-
fect of these additions on NiS is less than on NiO. A further observa-
tion of the authors is that only a single preparation was investigated
with 0.2 at% of Li so that the conformity of the result with that obtain-
ed by Yenikeyev may well be a matter of coincidence. There are 4 fig-
ures and 5 references: 4 Soviet and 2 German.

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Investigation of the Catalytic Decomposition of   S/020/60/133/02/46/068
Hydrazine on Nickel Sulfide and on Its Solid   B004/B064
Solutions

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
               (Institute of Physical Chemistry of the Academy of
               Sciences, USSR)

SUBMITTED: April 7, 1960

Card 4/4

ROGINSKIY, S. Z

S/020/60/133/03/11/013
B004/B056

AUTHORS: Khuan Yu-mey, Keyer, N. P., Roginskiy, S. Z., Corresponding
Member AS USSR

TITLE: Chemical Adsorption on Pure NiS and on NiS With Admixtures

TEXT: The authors investigated the chemical adsorption of oxygen and acetylene on pure NiS and on NiS with admixtures of Li_2S (0.2, 0.5, and 1.0 at% Li) and In_2S_3 (0.2, 0.5, and 1.0 at% In). The production of pure NiS and of NiS with admixtures has been described in an earlier paper. The adsorption was carried out in a vacuum apparatus, and the pressure drop of the gas introduced was measured. The adsorption of O_2 occurred at 25 - 65°C. It exerted no influence on electrical conductivity. Fig. 1a shows the kinetic isothermal lines of oxygen adsorption on pure NiS. They obey equation (1): $q = At^{1/n}$. The values of A and 1/n increase with

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.Chemical Adsorption on Pure NiS and on NiS With   S/020/60/133/03/11/013
Admixtures   B004/B056

rising temperature (Table 1). Fig. 1b shows the kinetic isochronous curve
$\log q_{t=const} = f(T)$, $(t = 30$ min). It obeys equation (2): $q = q_0 \exp(\beta T)$.
Equations (1) and (2) correspond to an inhomogeneous surface with an ex-
ponential distribution function (3): $\varrho(E) = H \exp(\alpha E)$. α and H are in-
dependent of temperature, and were calculated from the adsorption iso-
thermal lines: $\alpha \cong 0.69 \cdot 10^{-3}$ $(cal/mole)^{-1}$, $H \cong 1.1 \cdot 10^{-7}$ $(mole/cal)$. It
follows from Fig. 2 that admixtures of Li_2S and In_2S_3 decrease the
specific adsorption rate. Though the adsorption kinetics continues to
obey equation (1), the values for α and H are changed (Table 2). Li_2S
decreases the activation energy of O-adsorption, and In_2S_3 increases it.
The adsorption of acetylene was investigated at 100, 125, and $150^{\circ}C$.
Fig. 3a shows the kinetic isothermal lines of the adsorption of C_2H_2
on pure NiS in the coordinates $\log q$, $\log t$. Also in this case,
equation (1) continues to hold. Table 3 gives the values of A and $1/n$
which rise with temperature. Fig. 3b shows the isochronous curve of
C_2H_2 adsorption on pure NiS, for which equation (2) also holds. The
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Chemical Adsorption on Pure NiS and on NiS With   S/020/60/133/03/11/013

Admixtures   B004/B056

character of the kinetic isothermal lines is not changed by the admixtures (Fig. 4), but the adsorption rate is reduced both by Li_2S and In_2S_3. Table 4 gives the values for the activation energy E, calculated according to $E = RT \ln (t/t_0)$. E is decreased by Li_2S, whereas In_2S_3 causes no change. For the dependence of the adsorption energy E_{ads} on the degree of population of the surface, the equation $E_{ads} = 22.5 + 4.4 \log q$ kcal/mole is given, and for the distribution function of the active zones the equation $\varphi(E_{ads}) = 0.25 \cdot 10^{-8} \exp\left[0.55 \cdot 10^{-13}\right] \cdot E_{ads}$. There are 4 figures, 4 tables, and 8 references: 7 Soviet and 1 German.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences USSR)

SUBMITTED: April 14, 1960

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S/020/60/133/004/040/040XX
B004/B067

AUTHORS: Roginskiy, S. Z., Corresponding Member of the AS USSR,
Yanovskiy, M. I., Lu Pey-chzhan, Gaziyev, G. A., Zhabrova,
G. M., Kadenatsi, B. M., and Brazhnikov, V. V.

TITLE: Rapid Chromatographic Method of Measuring the Adsorption
Isotherms of Gases and Vapors

TEXT: Since in heterogeneous catalysis the dimensions of the specific
surface are of great importance, the authors attempted to develop a rapid
method of determining the specific surface. Their studies were based on a
paper by J. N. Wilson (Ref. 1) where the relation between the chromato-
graphic curve and the form of the isotherm is theoretically studied. The
results were compared with those of the ordinary vacuum technique. Fig. 1
shows the scheme of the experimental apparatus. The gas analyzer was an
ionization detector on the basis of Pm^{147} (Ref. 5). The adsorption of
heptane was measured. Nitrogen and sometimes argon were used as carriers.

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Rapid Chromatographic Method of Measuring the   S/020/60/133/004/040/040XX
Adsorption Isotherms of Gases and Vapors   B004/B067

The height of the steps recorded corresponds to the initial concentration C_0 of the adsorbate. The desorption curves recorded on blowing the pure carrier gas through the column permit the calculation of the isothermal line of adsorption. In a variation of this method, the column is not saturated, but the sample is periodically injected into the column through which the carrier gas flows. The experiment then lasts only 10-15 min. On the assumption of an immediately established equilibrium and the absence of longitudinal diffusion, the adsorption was calculated from the following equations: $f(C) = \omega k S_i / ug$ (2), where $f(C)$ is the amount of the substance adsorbed by 1 g of adsorbent (mmole/g) in which C is the equilibrium concentration; k is the constant of the detector (mmole/cm^3.cm); u is the speed of the recorder tape; g is the weight of the adsorbent (g); and S_i is the area below the desorption curve. The following adsorbents were used: refractory diatomite bricks, silica gel of the type E (Ye), nickel-hydroxide gel, nickel catalyst, MgO produced from $Mg(NO_3)_2$, $ZnO+14.5$ $ZnSO_4$,

and carbon black. The values for MgO, silica gel Ye, nickel hydroxide, and diatomite were in good agreement with those obtained by the vacuum technique. For adsorbents with a large number of very narrow pores (active

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Rapid Chromatographic Method of Measuring the   S/020/60/133/004/040/040XX
Adsorption Isotherms of Gases and Vapors   .   B004/B067

coal) the results were unsatisfactory. The range of application of the
chromatographic method must be further studied. The authors thank
I. Ye. Neymark and M. A. Piontrovskiy for preparing the coarse-pored
silica gel Ye and nickel-hydroxide samples. There are 4 figures, 1 table,
and 5 references: 2 Soviet, 1 US, 1 British, 1 Dutch, and 1 Hungàrian.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute
of Physical Chemistry of the Academy of Sciences USSR)

SUBMITTED: January 28, 1960
Legend to Fig. 1: 1: cylinder with carrier gas; 2: bubbler with adsorbate;
3: chromatographic column; 4: gas analyzer; 5: recording potentiometer;
6-10: fine-regulating valves; 11: four-way cock; 12-15: rheometers.

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S/020/60/133/004/040/040XX
B004/B067
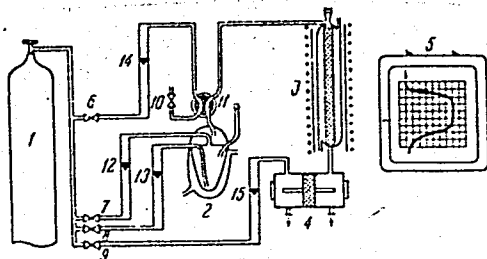
Card 4/4

84706

S/020/60/133/006/014/016
B004/B064

II. 1325

AUTHORS: Stepanov, Yu. N., Margolis, L. Ya. and Roginskiy, S. Z.,
            Corresponding Member AS USSR

TITLE: The Mobility of Modifying Admixtures in Silver

TEXT: In the introduction the authors discuss papers on the modification
of the catalytic activity of metals with admixture of small quantities
of metalloids (Refs. 1-13). In the present paper, they investigate the
behavior of admixtures, the change in their concentration, and their
escaping from the metal. Silver powder was tagged with Cl^{36}, I^{131}, or
S^{35} by adsorption of NaCl, KI, or Na_2SO_4, and then pressed to tablets.
The regularity of distribution of the admixture was examined with an end
window counter. The silver tablets were then heated with gas mixtures.
Fig. 1 shows that the heating of the tablets with air or nitrogen to
$300^\circ C$ did not bring about a change of the specific radioactivity, whereas

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The Mobility of Modifying Admixtures
in Silver

S/020/60/133/006/014/016
B004/B064

air with 3% ethylene reduced the radioactivity under the same conditions. The authors assumed that a reduction of chlorine to HCl takes place, and that all reducing agents containing hydrogen are bound to cause the same effect. The experimental data of Table 1 (reaction with H_2, C_2H_4, $N_2 + 5.3\%$ i-C_3H_7OH, $N_2 + 2\%$ C_2H_4O, CO) confirm this. Only CO proved not to reduce radioactivity. Further experiments were conducted to determine HCl in the reaction products. Silver tablets containing Cl^{36} were heated with C_2H_4 to $300^\circ C$. A silver tablet cooled to $40^\circ C$ stood at a distance of 15 cm. After five hours of experimenting the silver plate had become radioactive. The same effect was obtained with $S^{35}O_4^{2-}$. Absorbing the reaction products in water, containing methyl red, proved their acidity. HCl was nephelometrically determined with $AgNO_3$. Measurement of radio-activity in sections through the silver tablets proved that radioactivity decreased in the entire volume of tablets, i.e. that no surface reaction was concerned. The diffusion of chlorine ions by silver was proven on a silver single crystal with Cl^{36}. Fig. 2 shows the change of the radio-activity of Ag in various $N_2 + C_2H_4$ mixtures at $300^\circ C$, Fig. 3 log C (C

Card 2/3

STEPANOV, Yu.N.; MARGOLIS, L.Ya.; ROGINSKIY, S.Z.

Modification of a silver catalyst by organohalogen compounds.
Dokl. AN SSSR 135 no.2:369-372 N '60. (MIRA 13:11)

1. Institut fizicheskoy khimii AN SSSR. 2. Chlen-korrespondent
AN SSSR (for Roginskiy).
   (Catalysts) (Silver)

33484
S/195/61/002/005/009/027
E040/E385

5 1190 1273

AUTHOR: Roginskiy, S. Z.

TITLE: Kinetic isotope effects in simple and complex
reactions

PERIODICAL: Kinetika i kataliz, v. 2, no. 5, 1961, 694-704

TEXT: The kinetic isotope effect (KIE) is defined as any
change in the nature and velocity of the processes arising from
a change in the isotopic composition and structure of the
reactants and catalyst. As a measure of KIE is taken the ratio
α of the velocity constants (k) of the reaction of isotopic
molecules or their fragments: $\alpha_{12} = k_1/k_2 \sim v_1/v_2$, where
v_1 and v_2 are the respective reaction velocities. Starting
with the above definition, a theory is developed of KIE in com-
plex heterogeneous and homogeneous reactions, with special
emphasis on recent advances concerning the appearance of complex
stages in catalytic reactions and its influence on the develop-
ment of anomalous KIE in heterogeneous catalysis. Detailed
mechanisms are proposed for heterogeneous catalysis in the gas,

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33484

Kinetic isotope effects ....

S/195/61/002/005/009/027
E040/E382

surface and solid-body stages. The theory is illustrated with examples of H_2 and D_2 chemisorption on zinc oxide, distribution of various hydrocarbons in the products of synthesis in the presence of cobalt catalysts, as a function of the number of carbon atoms in the compounds produced in reactions involving two mixtures with different isotopic CO contents. Care is advocated in applying the theory of primary and secondary KIE of simple reactions to stage-wise reactions. In conclusion, attention is drawn to the possibility of applying KIE in investigations of active surfaces and the state of molecules adsorbed on active centres. The character and value of KIE should, for localised reactions, depend on the type of the actual chemical bond with the surface. Thus, the value of KIE could indicate whether, in the case of metals and semiconductors covered with thin layers of a non-metal (oxygen, nitrogen, etc.) chemisorption occurs invariably on Pt or Ni and not on Ga or some other chemisorptive film. In spite of the considerable practical

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S/195/61/002/005/009/027
E040/E382

Kinetic isotope effects .....

and theoretical difficulties associated with studies of the KIE
in catalytic reactions, the author regards the subject as very
promising for further investigations. S.E. Shnol' is
mentioned in the article in connection with his contributions
in this field. There are 1 figure and 9 references:
7 Soviet-bloc and 2 non-Soviet-bloc. The two English-language
references mentioned are: Ref. 2: R.P. Bell - Adv. catal.,
4, 151, 1952: Ref. 3: G. Parravano, H.G. Friederick,
M. Boudart - J. Phys. chem. 63, 1144, 1959.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR
                (Institute of Chemical Physics of the AS USSR)

Card 3/3

33485
S/195/61/002/005/010/027
E071/E435

//. /2 3 O
/4 /1 0 5

AUTHORS: Popov, V.I., Roginskiy, S.Z.

TITLE: Kinetic isotopic effect (KIEF) and the mechanism of
              oxidation of hydrogen on platinum

PERIODICAL: Kinetika i kataliz, v.2, no.5, 1961, 705-709

TEXT: In the authors' opinion, measurements of kinetic isotopic
effects of catalytic reactions during isotopic exchange in one or
more reacting components can provide information on the nature of
the controlling stage of the process and the structure of the
intermediate complex formed during this stage.   For this reason,
they measured the kinetic effect of oxygen on the basis of the
separation of a mixture of its isotopes during oxidation of hydrogen
on smooth platinum.   The reaction was carried out in the
temperature range -78 to 400°C.   As a catalyst, platinum wire of a
geometrical surface area of 30 cm^2 was used;   the mixture used
was $H_2:O_2 = 1:1$ with an initial pressure of about 0.3 mm Hg.   The
isotopic composition of the starting and unreacted oxygen was
determined with a mass spectrometer (relative accuracy $\pm$ 0.6%).
From the isotopic composition, the concentration of O^{18} in
oxygen of the water formed was calculated.   The degree of isotopic
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33485

S/195/61/002/005/010/027
E071/E435

Kinetic isotopic effect (KIEF) ...

separation was calculated from

$$ S = \frac{(O^{16})_{in\ water}}{(O^{18})_{in\ water}} : \frac{(O^{16})_{starting}}{(O^{18})_{starting}} $$

Oxidation of the unreacted oxygen resulted in some enrichment with the O^{18} isotope. The value of the kinetic isotopic effect of oxygen changes steadily with increasing temperature of the reaction from 1.05 at -78 °C to 1.01 at 400 °C. From the plot of log S against (1/T) the difference in the energy of activation $\triangle E$ of the reactions with $O^{16}O^{18}$ and O_2^{16} was calculated (the presence of O_2^{18}, the concentration of which in the mixture of isotopic oxygen molecules is by one order below that of $O^{16}O^{18}$ was neglected) as 20 + 10 cal/mole. $\triangle E_0$ calculated for isolated $O^{16} - O^{16}$ and $O^{16} - O^{18}$ bonds equals 60 cal/mole. Comparison of the above two values leads to the conclusion that the oxygen isotopic effect could be due to the kinetic stage of the oxidation of hydrogen in which the formation of an intermediate complex takes place only with some weakening of the bonds between oxygen atoms as Card 2/3
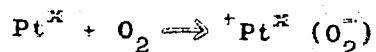
33485

S/195/61/002/005/010/027
E071/E435

Kinetic isotopic effect (KIEF) ...

compared to their original state and not their complete split.
The authors express the view that the controlling stage in the
oxidation of hydrogen is chemisorption of oxygen on activated
platinum:

$$Pt^x + O_2 \longrightarrow {}^+Pt^x (O_2^-)$$

Acknowledgments are expressed to I.I.Tretyakov for his advice.
There are 1 figure, 1 table and 8 references: 6 Soviet-bloc and
2 non-Soviet-bloc.   The reference to an English language
publication reads as follows: Ref.2: L.C.S.Melander,   Isotope
Effects on Reaction Rate. Ronald Press, N.Y., 1960.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR
             (Institute of Chemical Physics AS USSR)

Card 3/3

20112

9.4300 (and 1035, 1143)

AUTHORS: Kushnerev, M. Ya., Linde, V. R., and Roginskiy, S. Z.

TITLE: The electric conductivity of cobalt-manganese spinels with additions of lithium-, titanium- and copper oxides

PERIODICAL: Fizika tverdogo tela, v. 3, no. 2, 1961, 384-394

TEXT: After a detailed discussion of Western publications, the present paper deals with the results obtained by studying the structure and the electric conductivity of "direct" $(CoMn_2O_4)$ and "inverse" $(MnCo_2O_4)$ cobalt-manganese spinels with Li-, Ti- and Cu admixtures. $CoMn_2O_4$ is a nearly direct tetragonal spinel with the parameters $a = 5.72$ kX, $c = 9.29$ kX, the parameters of the oxygen anion $x = 0.327$, $z = 0.365$ and a cation distribution (per unit cell):

$Co_{6.8}^{2+}Mn_{1.2}^{3+}\left[Co_{1.2}^{2+}Mn_{4.8}^{3+}\right]O_{32}^{2-}$. $MnCo_2O_4$ is a purely "inverse" cubic spinel with the parameters $a = 8.27$ kX, $u = 0.382$ and the cation distributions

a) $Co_8^{3+}\left[Mn_8^{2+} Co_8^{3+}\right]O_{32}^{2-}$ or b) $Co_8^{2+}\left[Mn_8^{4+} Co_8^{2+}\right]O_{32}^{2-}$. The composition of the

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The electric conductivity of....

S/181/61/003/002/010/050
B102/B204

specimens investigated is given in the table. The specimens were obtained
by heating of spinel powder with the corresponding oxides in corundum
crucibles in air at 1200°C for 2 hr. The agglomerate obtained was again
finely ground and heated under the same conditions, after which it was
slowly cooled to room temperature. The alloys obtained were first
subjected to X-ray examination. The electric conductivity of the speci-
mens pressed to 24·8·8 mm tablets was investigated within the range of
100-600°C by means of d.c. probes; the measurements were carried out in
quartz vacuum cells. The specimens were first heated in the cells at
10^{-6} mm Hg at 650°C for 2 hr, after which pure argon was introduced (up
to 5 mm Hg); in this atmosphere the specimens remained till temperature-
and resistance equilibrium had been established; only then were the
measurements carried out. Control measurements were carried out at
higher and lower temperature. The measured values obtained were trans-
lated into specific value. The X-ray structural investigations produced
the following result: Li-admixtures to a "direct" spinel caused the
reconstruction of the tetragonal lattice to a perturbed cubic spinel with
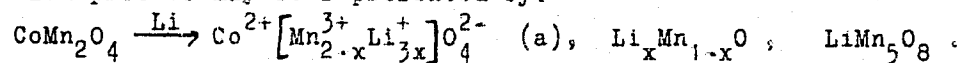parameters similar to the "inverse" spinel. If one assumes that the

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B102/B204

The electric conductivity of...

Li-atoms replace part of the Mn-cations in octahedral order, this substitution process may be represented by:

$$CoMn_2O_4 \xrightarrow{Li} Co^{2+}[Mn^{3+}_{2-x}Li^+_{3x}]O^{2-}_4 \quad (a), \quad Li_xMn_{1-x}O , \quad LiMn_5O_8 .$$

Radiographically, the line of the spinel $LiMn_5O_8$ could be determined. With the introduction of Li into the cubic lattice of the "inverse" spinel, the tetragonal distortion of the lattice increases; a decreases linearly with growing Li-concentration. Li^+ in octahedral order substitutes Mn^{2+}:

$$Co^{3+}[Mn^{2+}_{1-x}Li^+_{2x}Co^{3+}]O^{2-}_4 \quad (b). \quad In the final result a Li-Co phase of the$$
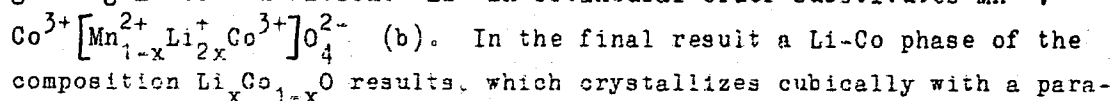
composition $Li_xCo_{1-x}O$ results, which crystallizes cubically with a parameter of about 4.2 A. An addition of 5% titanium to a "direct" spinel causes a considerable disturbance of the tetragonal lattice, without, however, a new phase occurring; higher additions cause a re-formation of the lattice to rhombohedral structure when an ilmenite-type lattice compound is formed. With 51.4% titanium, the spinel phase vanishes completely, and small vestiges of titanium oxide occur. Analogous phenomena occurred with an addition of titanium to an "inverse" spinel. In general
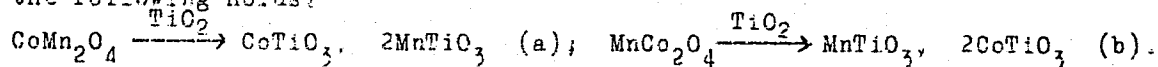
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S/181/61/003/002/010/050
B102/B204

The electric conductivity of....

the following holds:

$$CoMn_2O_4 \xrightarrow{TiO_2} CoTiO_3, \quad 2MnTiO_3 \quad (a); \quad MnCo_2O_4 \xrightarrow{TiO_2} MnTiO_3, \quad 2CoTiO_3 \quad (b).$$

An addition of copper to "direct" spinel causes the forming of a solid substitution solution. A re-formation of the tetragonal lattice to a cubic lattice according to

$$CoMn_2O_4 + CuO \begin{cases} CuMn_2O_4 \\ MnCo_2O_4 \end{cases} \quad (distorted)$$
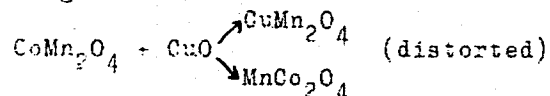
occurs. The "inverse" spinel reacts quite differently with CuO: Up to 25 at% Cu, no chemical reaction at all occurs between $MnCo_2O_4$ and CuO. All specimens (no. 19, 20, 21) showed lines of the pure, very weakly deformed $MnCo_2O_4$, of copper oxide and of cuprous oxide. The results obtained by measurements of electric conductivity are shown in Figs. 3 and 4. As may be seen, the introduction of additions to "inverse" spinels produces no qualitative effect upon $\sigma(T)$; also the activation energy of conductivity remains constant. All spinels investigated were p-type semiconductors.

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The electric conductivity of...

S/181/61/003/002/010/050
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The $\sigma(T)$-measurements of all specimens showed that the mechanism of the electric conductivity of the complex spinels cannot be brought into line with the model by Verwey. As regards the effect produced by the various admixtures it is not the structural change that produces an essential effect upon the electric properties of the spinels, but the valence state and the chemical composition of its cationic components. The authors finally thank A. I. Zaslavskiy for discussions and V. F. Shustov for his help. K. P. Belov, Ye. V. Talalayeva, and B. T. Kolomiyets are mentioned. There are 5 figures, 1 table, and 17 references: 5 Soviet-bloc and 6 non-Soviet-bloc.

ASSOCIATION: Institut fizicheskoy khimii AN SSSR Moskva (Institute of Physical Chemistry of the AS USSR, Moscow)

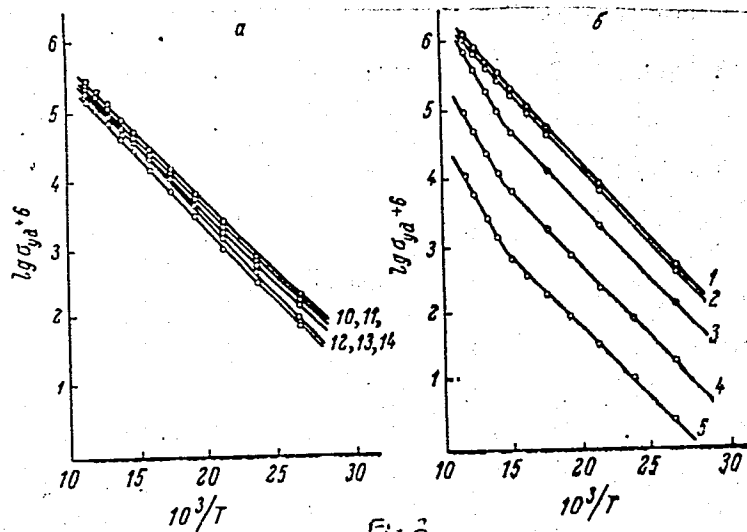SUBMITTED: April 8, 1960 (initially) and October 1, 1960 (after revision)

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20112

The electric conductivity of...

Legend to the figures:
The numbers beside the
straight lines are the
numbers of the specimens.
The ordinate is log σ + 6,
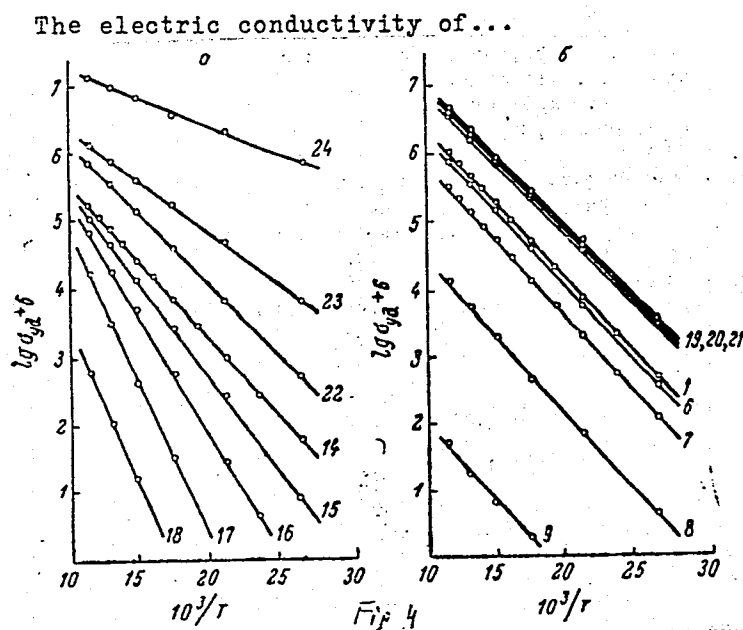where σ is the specific
electric conductivity.

Fig 3

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S/181/61/003/002/010/050
B102/B204

The electric conductivity of...

Fig. 4

$lg\,\sigma_{yd} + 6$

$lg\,\sigma_{yd} + 6$

$10^3/T$

$10^3/T$

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B102/B204

The electric conductivity of...

1 Номер шпинели (рис. 1)	2 Прямая шпинель	1 Номер шпинели (рис. 1)	3 Обратная шпинель
14	$CoMn_2O_4$	1	$MnCo_2O_4$
10	$CoMn_2O_4 + 5.2Li$	2	$MnCo_2O_4 + 5.4Li$
11	$CoMn_2O_4 + 21.4Li$	3	$MnCo_2O_4 + 22.0Li$
12	$CoMn_2O_4 + 35.4Li$	4	$MnCo_2O_4 + 36.0Li$
13	$CoMn_2O_4 + 45.0Li$	5	$MnCo_2O_4 + 46.0Li$
15	$CoMn_2O_4 + 5.3Ti$	6	$MnCo_2O_4 + 5.5Ti$
16	$CoMn_2O_4 + 10.4Ti$	7	$MnCo_2O_4 + 11.0Ti$
17	$CoMn_2O_4 + 26.5Ti$	8	$MnCo_2O_4 + 27.0Ti$
18	$CoMn_2O_4 + 51.4Ti$	9	$MnCo_2O_4 + 52.5Ti$
22	$CoMn_2O_4 + 5.0Cu$	19	$MnCo_2O_4 + 5.0Cu$
23	$CoMn_2O_4 + 10.0Cu$	20	$MnCo_2O_4 + 10.0Cu$
24	$CoMn_2O_4 + 25.0Cu$	21	$MnCo_2O_4 + 25.0Cu$

Legend to the table: 1) no. of specimen; 2) "direct" spinel; 3) "inverse" spinel.

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S/020/61/136/004/020/026
B028/B060

AUTHORS: Linde, V. R., Margolis, L. Ya., and Roginskiy, S. Z.,
            Corresponding Member AS USSR

TITLE: Catalytic Properties of Cobalt - Manganese Spinels

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 4,
            pp. 860-863

TEXT: The present paper deals with the effect of the structure of spinels
$CoMn_2O_4$ and $MnCo_2O_4$ upon the catalytic action in propylene oxidation.
The catalytic activity was determined by measuring the oxidation rate of
propylene with O_2 in a stoichiometric ratio of $C_3H_6:O_2 = 2:9$. The reaction
product contained CO_2 gas and water. The specific surface of the catalyst
was determined by the BET method from the equilibrium isotherms of
krypton sorption. The specific surface was 0.70 m^2/g for $CoMn_2O_4$ and
0.25 m^2/g for $MnCo_2O_4$. The reaction took place at a constant initial
mixture pressure of 0.450 mm Hg and in the temperature range of
200° – 350°C. For purification, catalyst specimens were heated in vacuo —

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Catalytic Properties of Cobalt - Manganese   S/020/61/136/004/020/026
Spinels   B028/B060

(10^{-6} mm Hg) at $550°$ for 4 hours. The resulting water was frozen out. CO_2 was removed by absorption. The reaction kinetics obeys a monomolecular law. The diagram of Fig. 1 with the coordinates log P = $f(\tau)$ contains the kinetic isothermal lines for the oxidation of the $2C_3H_6+9O_2$ mixture on $MnCo_2O_4$ at $250°C$. On the assumption of a monomolecular law, they have a linear course, while the assumption of a square dependence leads to distortion. CO_2 molecules probably form complexes of the type CO_3^- on the catalyst surface. The specific rate constant K^I calculated by a reaction equation of the 1st order remains steady (Fig. 2). For a $2C_3H_6+9O_2$ oxidation at different temperatures, without removal of CO_2, the total velocity may be calculated approximately with a reaction equation of the 2nd order. The specific constant K^{II}, referred to surface unit of $1m^2$ catalyst, was found for each temperature. K^{II} is a function of the initial pressure of the mixture. The reaction rate was found to be independent of the propylene concentration. An increase of the O_2 content from 0.096 to 0.433 mm Hg leads to an increase of the reaction rate. The latter depends on the O_2 concentration according to equation

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Catalytic Properties of Cobalt - Manganese Spinels

S/020/61/136/004/020/026
B028/B060

$W = K^I [P_{O_2}]^1 [P_{C_3H_6}]^0$. It has been earlier pointed out that O_2 undergoes a chemically irreversible sorption on both spinels, the kinetics of chemosorption obeying equation $\theta = A\tau^{1/n}$ for $MnCo_2O_4$ and $\theta = a+b \log\tau$ for $CoMn_2O_4$. θ = occupation of surface, τ = time. Measurements of chemosorption of O_2 on both spinels yielded the following values for the activation energy: 18 kcal/mole for $CoMn_2O_4$ and 14 kcal/mole for $MnCo_2O_4$ for $\theta = 0.03$ cm^3/m^2, temperature range 200^0-350^0C. The problem as to whether oxidation takes place by a homogeneous or a heterogeneous mechanism, was studied by the method of the separate calorimetric procedure devised by A. A. Koval'ckiy and M. L. Bogoyavlenkaya (Ref. 9).The reaction vessel was 50 mm in diameter. A nichrome constantan differential thermocouple was used for the measurement of the temperature difference. For both catalysts oxidation took place on the surface at 300^0 and a pressure of 0.5 and 40.0 mm Hg over a purely heterogeneous mechanism. The structural formula of the spinels $Co^{2+}(Mn^{3+}Mn^{3+})O_4^{2-}$ and $Co^{3+}(Mn^{2+}Co^{3+})O_4^{2-}$ shows that Mn cations present on the surface constitute more intense electron donors for oxygen atoms undergoing sorption, than Co cations. There are 4
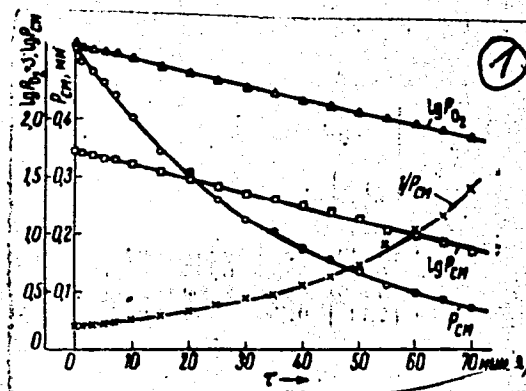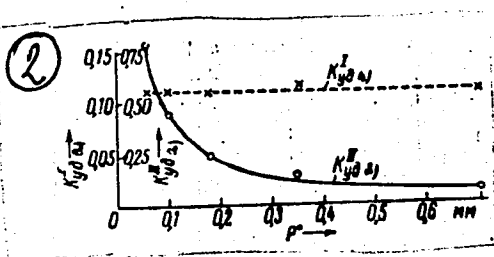
Card 3/5

Catalytic Properties of Cobalt - Manganese
Spinels

S/020/61/136/004/020/026
B028/B060

figures, 2 tables, and 14 references: 10 Soviet, 1 German, 1 British, and
1 Polish.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute
of Physical Chemistry, Academy of Sciences USSR)

SUBMITTED: October 19, 1960

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S/020/61/136/004/020/026
B028/B060
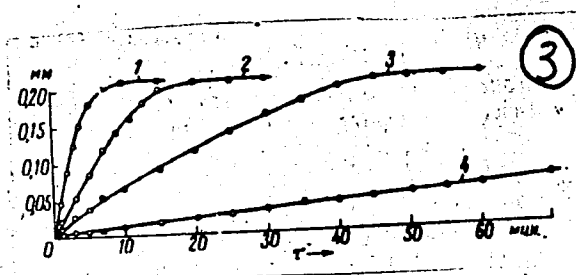
Legend to Fig. 1: Kinetic isotherms for the oxidation of $2C_3H_6 + 9O_2$ at 250°C. $P^o = 0.522$ mm Hg, a) minutes.

Legend to Fig. 2: Dependence of specific rate constants K^I K^{II} on the initial pressure P_o, a) = spec.

Legend to Fig. 3: Kinetic isotherms for oxidation on $CoMnO_4$
1=350°C, S=0.14 m^2; 2=300°C, S=0.25 m^2; 3=250°C, S=0.50 m^2; 4=200°C, S=0.50 m^2 a) minutes b) mm.

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GORDEYEVA, V.A.; YEGOROV, Ye.V.; ZHABROVA, G.M.; KADENATSI, B.M.;
    KUSHNEREV, M. Ya.; ROGINSKIY, S.Z.

Use of ionizing radiation in the study of the decomposition
processes of copper and nickel oxalates. Dokl. AN SSSR 136
no.6:1364-1367 F '61.   (MIRA 14:3)

1. Institut fizicheskoy khimii AN SSSR. 2. Chlen-korrespondent
AN SSSR (for Roginskiy).
                        (Copper oxalate)
                        (Nickel oxalate)
                         (Radiation)

ROGINSKIY, S.Z.; SHNOL', S.E.

Feasible explanation of anomalous biological isotopic effects observed in D_2O^{16} and H_2O^{18}. Dokl. AN SSSR 137 no.3:706-709 Mr '61. (MIRA 14:2)

1. Chlen-korrespondent (for Roginskiy).
   (Water—Physiological effect)   (Oxygen—Isotopes)
                   (Deuterium oxide)

21400   S/020/61/137/004/025/031
B101/B208

2209, 1208, 1207

5,1190

AUTHORS: Dokukina, Ye.S., Roginskiy, S.Z., Corresponding Member AS
USSR, Sakharov, M.M., Topchiyev, A.V., Academician,
Geyderikh, M.A., Davydov, B.E., and Krentsel', B.A.

TITLE: Catalysis on organic semiconductors obtained by heat
treatment of polyacrylonitrile

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 4, 1961, 893- 895

TEXT: It could be assumed on the basis of the bibliography and the ge-
nerally accepted concept of the catalytic meachanism that organic semicon-
ductors with small forbidden band width and considerable electrical con-
ductivity at room temperature should be active catalysts in redox reac-
tions.   Only qualitative data being available so far, it was the purpose
of this study to investigate the catalytic activity of polymer semicon-
ductors containing a system of conjugate bonds on redox reactions in the
gaseous and vapor phases.   The authors have chosen semiconductors from
polyacrylonitrile (PAN). Data on preparation and electrical properties of
this material are given in Ref. 7 (A.V. Topchiyev, M.A. Geyderikh et al.,

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B101/B208

Catalysis on organic ...

DAN, 128, 312 (1959)), and have been reported by M.A. Geyderikh at the International Symposium on Macromolecular Chemistry on June 14 - 18, 1960. Two PAN samples were used: PAN-1 to which 0.01% $CuCl_2$ was added prior to heat treatment, and which had a specific surface of 0.06 m^2/g (determined by means of krypton), and PAN-2 without copper admixture and with a specific surface of 0.04 m^2/g. Catalytic activity was studied in an apparatus similar to that of G.M. Schwab, N. Theophilides (Ref. 13, see below). The catalysts were annealed at 450°C for 1-3 hr prior to the experiment. Considerable catalytic activity was only observed in the decomposition of formic acid. Experimental data are given in Table 1. The copper admixture was found to be of minor importance. As the change of the decomposition rate v of HCOOH was determined by the continuous method on a stepwise rise o' temperature, a constant rate of acid addition, and a low degree of conve sion (1 - 10%), the activation energy could be calculated from log v = f(1/T). It was 21 kcal for PAN-1, and 25 kcal for PAN-2. The catalytic activity of the samples increased from experiment to experiment until it reached a constant value. Activation energy, however, remained nearly constant. A catalytic action of PAN on the decomposition of hydrazine hydrate

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B101/B208

Catalysis on organic ...

in NH_3 and N_2 was observed only at high temperatures (250°C) at which the reaction on the glass surface of the vessel and homogeneous decomposition play an important role. The specific activity of PAN with respect to the decomposition of HCOOH is explained by its chemical structure. The N-atoms in the chain of the conjugate bonds are assumed to act as adsorption centers for the acid molecules. By changing the chemical and electrophysical properties of polymers with conjugate double bonds, highly selective catalysts should be obtained which are comparable to those used in fermentative catalysis. This is the reproduction of a report delivered by S.Z. Roginskiy, Corresponding Member AS USSR, before the Uchenyy Sovet Instituta khimicheskoy fiziki Akademii nauk SSSR (Scientific Council of the Institute of Chemical Physics of the Academy of Sciences USSR) on May 27, 1960. Mention is made of A.A. Berlin, L.A. Blyumenfel'd, N.N. Semenov. (Ref. 11: Izv. AN SSSR, OKhN, 1959, no. 9, 1689). There are 1 figure, 2 tables, and 14 references: 8 Soviet-bloc and 6 non-Soviet-bloc. The 3 references to English language publications read as follows: K. Tamaru, T. Shimada, Bull. Chem. Soc. Japan, 31, 141, (1958); D.D. Eley, Res. appl. Ind. 12, 293 (1959); G.M. Schwab, N.

Card 3/5

£1500
S/020/61/137/004/025/031

Catalysis on organic...   B101/B208

Theophilides, J. phys. Chem., 50, 427 (1946).

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
               (Institute of Physical Chemistry, Academy of Sciences
               USSR), Institut neftekhimicheskogo sinteza Akademii nauk
               SSSR (Institute of Petrochemical Synthesis of the Academy
               of Sciences USSR)

SUBMITTED: December 24, 1960

Card 4/5

Catalysis on organic ...

Table 1: Results of experiments on the decomposition of formic acid on PAN-1 and PAN-2. Legend:
(1) Number of experiment; (2) temperature, $^\circ$C; (3) formation rate of gaseous products, ml/hr;
(4) H_2/CO ratio; (5) rate of addition of formic acid vapor;
(a) PAN.

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Таблица 1
Результаты опытов по разложению муравьиной кислоты над ПАН-1 и ПАН-2

№ опыта	Т-ра, °C	Скорость образования газообр. прод., мл/час	Соотношение H₂:CO	Скорость подачи паров кислоты, мол. на 1 г кат. в час
ПАН-1				
3—1	242	153	2,8	0,02
3—2	255	265		
3—3	272	494		
ПАН-2				
6—1	260	66	3,2	0,3
6—2	287	232		
6—3	299	402		
6—4	261	86		
7—1	264	114	3,6	0,3
7—2	288	302		
7—3	304	554		
8—1	290	336	—	0,3

GAZIYEV, G.A.; KRYLOV, O.V.; ROGINSKIY, S.Z.; SAMSONOV, G.V.; FOKINA, Ye.A.;
YANOVSKIY, M.I.

Dehydrogenation of cyclohexane on certain carbides, borides, and
silicides. Dokl. AN SSSR 140 no.4:863-866 O '61.   (MIRA 14:9)

1. Chlen-korrespondent AN SSSR (for Roginskiy).
            (Cyclohexane) (Dehydrogenation) (Catalysts)

ROGINSKIY, S.Z.; YANOVSKIY, M.I.; GAZIYEV, G.A.

Chemical reactions under chromatography conditions. Dokl.
AN SSSR 140 no.5:1125-1127 O '61.   (MIRA 15:2)

1. Institut khimicheskoy fiziki AN SSSR. 2. Chlen-korrespondent
AN SS.R (for Roginskiy).

29818
S/020/61/140/006/015/030
B103/B101

5.5600

AUTHORS: Al'tshuler, O. V., Vinogradova, O. M., Roginskiy, S. Z.,
             Corresponding Member AS USSR, and Yanovskiy, M. I.

TITLE: Preparation of high-purity hydrocarbons by the method of
             thermo-desorption chromatography

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 6, 1961, 1307-1309

TEXT: The applicability of thermo-desorption chromatography to preparative
uses was studied. Isolation and purification of propylene was selected as
example. The methods were studied by M. I. Yanovskiy, S. N. Oziraner, and
Lu P'ei - chang (ZhPKh, 33, 1084 (1960)). The laboratory apparatus used
consisted of adsorption columns connected in series, which were filled
with the same or different sorbents. After a certain section of the
adsorption layer had been saturated by the mixture of the gases to be
separated, the columns were immersed gradually into an oven heated to
200-220°C. It was not possible to obtain complete desorption of propylene

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S/020/61/140/006/015/030
Preparation of high-purity ...   B103/B101

at temperatures below 200°C. At higher temperatures, secondary reactions
may occur in the heated zone. Gas samples were taken at the column outlet
and their composition was determined chromatographically. Helium was used
as inert carrier gas. A katharometer or an ionization detector with a
Pm source were used to detect the components of the mixture. Coarse and
close-grained silica gels and alumo gels of various types as well as
active carbon were used as adsorbents. 10 - 20 liters of the mixture could
be separated with a sorbent volume of 1 liter and a temperature of -20 to

-30°C of the cold section of the column. The content of propylene in the
initial mixtures was varied from 25 to 98%. Moreover, they contained
different volumes of ethane, propane, ethylene, acetylene, and hydrocarbons
boiling higher than propylene, as well as H_2O and sulfur-containing

compounds. First, the partition capacity of the sorbents for the mixture
of propylene and one of these components was determined. It was
characterized by the ratio $V_{R\ comp}/V_{R\ C_3H_6}$. Based on these values $\left(V_{R\ rel}\right)$

suitable sorbents and their sequence for isolating the propylene from the
mixture were selected. The effect of the sorbents is shown in Table 1:
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Preparation of high-purity ...

Sorbent	admixture to be removed
active carbon	heavy hydrocarbons (boiling point $> 50°C$), CS_2, mercaptans, acetylene, ethylene, ethane, H_2S
silica gel	propane, carbon sulfochloride, ethane, ethylene, CS_2
alumo gel	ditto + CH_2 and H_2O

It has been established that the less sorbable components, such as air, ethane, ethylene, and propane, concentrate in the first fractions; thereafter, only propylene is found at the column outlet. In the ultimate gas samples desorbed by heating the column end, admixtures were found which were more intensively sorbed than propylene. The use of the highly sensitive detector revealed that the admixture of propane, the separation of which from propylene is most difficult, can be reduced to traces. Thus, it is possible to obtain pure propylene even from initial mixtures poor in propylene.

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The purification coefficients do not become worse, when passing to the
range of propylene with very low admixture concentrations. This is an
advantage of the present alternative as compared with the rectification,
since it ensures a very high degree of purification. Unlike in development
chromatography, the components are isolated undilute in thermo-desorption
chromatography. Moreover, this method can be applied to obtain further
components of the mixture in pure state (e. g., benzene, cyclohexane). The
paper by Ye. V. Vagin, Gazovaya khromatografiya, Tr. I Vsesoyuzn. konfer.,
Izd. AN SSSR, 1960, p. 118, is mentioned. There are 4 figures and 3 Soviet
references.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR
               (Institute of Chemical Physics of the Academy of Sciences
               USSR)

SUBMITTED: June 23, 1961

Card 4/4

ROGINSKIY, Simon Z.

"Calculation of zero energies."

CHEMISTRY (PHYSICAL), SOCIETY OF (French) - 12th Annual Meeting -
Paris, France, 4-8 Jun 62

Institute of Physical Chemistry, Academy of Sciences USSR

S/844/62/000/000/115/129
D207/D307

AUTHORS: Roginskiy, S. Z., Zhabrova, G. M., Gordeyeva, V. A.,
            yegorov, Ye. V., Kadenatsi, B. M. and Kushnerev, M. Ya.

TITLE: The use of ionizing radiation in investigation of topo-
            chemical processes

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khi-
            mii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962,
            668-673

TEXT: A study was made of the differences between the topochemical
processes of thermal decomposition and of decomposition, using 0.6
- 2 Hev electrons. The substances decomposed were copper oxalate
$(CuC_2O_4 \cdot 1/2H_2O)$ and nickel oxalate $(NiC_2O_4 \cdot 2H_2O)$ which were pre-
pared by precipitating nitrate solutions with oxalic acid at $50^\circ C$;
the samples were in the form of thin layers of powder. Thermal de-
composition in vacuum at $280^\circ C$ yielded 85% Cu + 15% Cu_2O and 95%
Ni + 2.0% NIO + 3% undecomposed residue. Thermal decomposition in
air at about $300^\circ C$ yielded 50% CuO + 50% Cu_2O and 100% NiO. Elec-

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The use of ionizing ...   S/844/62/000/000/115/129
                                           D207/D307

tron irradiation (3.6×10^9 - 3.3×10^{10} rad) at 100°C yielded usu-
ally pure metals with large (10 - 40%) residues undecomposed oxa-
lates; the metal yield increased with the radiation dose. Strong
preliminary irradiation (at least 0.6×10^9 rad) accelerated strong-
ly the subsequent thermal decomposition in vacuum. The mechanisms
of thermal and electron-bombardment decomposition were the same;
holes generated by heat or irradiation neutralized partly or com-
pletely the double charged oxalate ions which then moved to the
surface and were emitted as CO_2; electrons also generated by heat
or irradiation neutralized the doubly charged metal cations which
yielded pure metals. Oxides were formed as an intermediate stage
in the production of pure metals; in air, oxides were produced al-
so by oxidation of the pure metal products. The essential differ-
ence between electron bombardment and heat lay in the greater car-
rier-generation efficiency of the former. There are 2 figures and
1 table.

ASSOCIATION: Institut fizicheskoy khimii AN SSSR (Institute of
               Physical Chemistry, AS USSR); Institut khimicheskoy fi-
Card 2/2   ziki AN SSSR (Institute of Chemical Physics, AS USSR)

ROGINSKIY, S.Z.; YANOVSKIY, M.I.; GAZIYEV, G.A.

Catalytic reactions and catalysts under chromatographic investiga-
tion conditions. Kin.i kat. 3 no.4:529-540 Jl-Ag '62.
(MIRA 15:8)

1. Institut khimicheskoy fiziki AN SSSR.
(Catalysis) (Gas chromatography)

S/186/62/004/001/003/008
E075/E436

21.7200 (also 1558)

AUTHORS: Roginskiy, S. Z., Todes, O.M.,

TITLE: Physico-chemical features of the dynamic sorption of
radioactive materials

PERIODICAL: Radiokhimiya, v.4, no.1, 1962, 39-44

TEXT: The authors consider the systems in which the irreversible
adsorption of a radioactive species takes place, with the nuclear
transformation products not being sorbed. In such cases, it is
assumed that each occupied site of the adsorbent is freed when the
transformation of the adsorbed atom takes place. As an example
the chemisorption of radioactive Cl is considered. Cl being
transformed into Ar which is almost completely retained in solution.
A simplified analysis of the system shows that in the first stages
of sorption, space concentration of the radioactive Cl(Co)
decreases exponentially along the length of the column.   Distance
δ at which the concentration is halved is approximately $\delta = U/K$.
where   U is the space velocity of the gaseous stream and K is a
value characterizing the rate of sorption and represents the
reciprocal time of removal of the radioactive gas by the sorbent.
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Physico-chemical features ...

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Ratio of concentration C_B of Cl in the gas leaving the column to initial concentration C_o is

$$\frac{C_B}{C_o} = \exp\left(-\frac{x}{\delta}\right) \cong \exp\left(-\frac{Kx}{U}\right) \tag{6}$$

where x is the full length of the adsorbent column. Since the rate of sorption is very high, width of the zone of concentration fall δ is many times smaller than length of the column x and consequently, C_B is many times smaller than C_o. In the second stage of the process a front of the adsorbate is formed and the expression for length of the active layer of the column is as follows:

$$L_m \cong \frac{v_o}{\lambda} \cong \frac{UC_o}{\lambda N_o} \tag{13}$$

where v_o is initial velocity of the front movement, λ is a constant for the disintegration of Cl and N_o is the maximum quantity of gas which can be retained by a unit volume of the

Card 2/3

Physico-chemical features ...

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column.   When the front of the adsorbate ceases to move the final
distribution of Cl concentration is established in all the column.
The part of the column from the initial section to $x = L_m$
is practically saturated and the concentration in the gaseous
phase falls to $CL \simeq b_0$.   Below this layer the concentration falls
exponentially.   Thus the final concentration of Cl in the eluent
is approximately

$$\frac{c_B}{c_o} = \exp \left[- \frac{(x - L_m)}{\delta} \right] \qquad (15)$$

Therefore, for practically complete removal of radioactive gas,
the length of the adsorbent column   x   should not exceed double
length of the main operating length $x = 2L_m$.   Conditions
approximating those considered above may be encountered in the
movement of air containing pure isotopic radioactive halogens
through rocks and soil.   There are 3 figures.

SUBMITTED: January 12, 1961

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38521

S/186/62/004/003/017/022
E075/E436

5.5500

AUTHORS: Jech, Č., Zhabrova, G.M., Roginskiy, S.Z., Shibanova, M.D.

TITLE: The change of emanation capacity and the evolution of surface gaseous marker during dehydration of hydroxides

PERIODICAL: Radiokhimiya, v.4, no.3, 1962, 355-364

TEXT: The authors studied the processes of dehydration of metal hydroxides leading to changes in their structure and specific surface, using the classical emanation method with Th^{228}, as well as the method developed by one of the present authors (Č. Jech. Radioisotopes in Scientific Research. (Proc. First UNESCO Internat. Confer)., v.2, 491. London, Pergammon Press, 1958).   In the latter method inert radioactive marker gases are introduced into a solid by bombarding its surface with the gaseous ions in a high frequency electric discharge.   Thermogravimetric and X-ray analyses were also used.   The hydroxides studied were $Zn(OH)_2$, $Ni(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, $Zr(OH)_4$ and $Th(OH)_4$. The hydroxides were heated up to $600°C$.   The radioactive methods indicated the initiation of the dehydration processes with great

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ROGHINSKI, S.Z. [Roginskiy, S.Z.]

    Isotopic kinetic effects of the simple and complex reactions. Analele chimie 17 no.3:118-130 Jl-S '62.